

Counterion and pH-Mediated Structural Changes in Charged Biopolymer Gels

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A major focus of our research over the years has concerned the basic physical properties of polyelectrolyte gels using a variety of experimental techniques (e.g., small-angle neutron and X-ray scattering, static and dynamic light scattering, macroscopic osmotic and mechanical measurements) probing structure and interactions over a broad range of length and time scales, from 10 Å to the macroscopic scale and from 100 ns to 10 s, respectively. We found that in polyelectrolyte gels swollen in near physiological salt solutions volume transition may arise due to small changes in the concentration of the counterions in the solution. It has also been demonstrated that the polyelectrolyte chains are surrounded by a sheath of oppositely charged counterions. Recent experimental observations made by anomalous small-angle X-ray scattering indicate that the spatial extent of the counterion cloud is significantly reduced when monovalent ions are replaced by divalent ions. The preferential condensation of divalent counterions is accompanied by an increase of the translational entropy of monovalent counterions and by a decrease of the electrostatic energy of the system.

In the present study we compare the effects of pH and calcium ions on the osmotic pressure and the small-angle neutron scattering response of anionic polyelectrolyte gels. Specifically, we investigate the behavior of poly(acrylic acid) and DNA gels. In these gels volume transition can be induced (i) by decreasing the pH, and (ii) by increasing the concentration of multivalent counterions. A thermodynamic framework is used to describe the effect of ions on the osmotic properties. The total free energy of the swollen network is represented as the sum of a mixing entropy term and an elastic term. Analysis of the osmotic pressure data reveals significant differences between the thermodynamics of pH and ion-exchange induced volume transitions. Small-angle neutron scattering is used to detect ion-mediated changes in the gel structure. The effect of ions on the characteristic length scales that govern the osmotic concentration fluctuations is determined.

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